CONTROL OF THE COMPOSITION OF ELECTRODEPOSITED ALLOYS
BY THE USE OF CERTAIN TYPES OF ADDITIVES

Thomas C. Franklin, Venita Totten,
Ali I. Aktan and Danielle Beu

January 1989

U. S. Army Research Office
Contract Number DAAG 29-85-K-0205

Baylor University

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REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified		1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY		3 DISTRIBUTION / AVAILABILITY OF REPORT Approved for public release; distribution unlimited.		
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE				
4. PERFORMING ORGANIZATION REPORT NUMBER(S)		5. MONITORING ORGANIZATION REPORT NUMBER(S) ARO 22727.13-CH		
6a. NAME OF PERFORMING ORGANIZATION Baylor University Chemistry Department	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION U. S. Army Research Office		
6c. ADDRESS (City, State, and ZIP Code) Baylor University Chemistry Dept. B. U. Box 7348 Waco, TX 76798		7b. ADDRESS (City, State, and ZIP Code) P. O. Box 12211 Research Triangle Park, NC 27709-2211		
8a. NAME OF FUNDING / SPONSORING ORGANIZATION U. S. Army Research Office	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER Contract No. DAAG 29-85-K-0205		
8c. ADDRESS (City, State, and ZIP Code) P. O. Box 12211 Research Triangle Park, NC 27709-2211		10. SOURCE OF FUNDING NUMBERS		

		PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO

11 TITLE *(Include Security Classification)*

Control of the Composition of Electrodeposited Alloys by the Use of Certain Types of Additives (Unclassified)

12. PERSONAL AUTHOR(S)
Thomas C. Franklin, Venita Totten, Ali I. Aktan and Danielle Beu

13a. TYPE OF REPORT Final	13b. TIME COVERED FROM 8/1/85 TO 12/31/88	14. DATE OF REPORT (Year, Month, Day) Feb 13, 1989	15. PAGE COUNT 59

16. SUPPLEMENTARY NOTATION The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

17.	COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Additive, Electrodeposition, Mechanism, Alloys, Ion pairing, Electron Bridging, Electrode Filming.

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Using the principle that additives used in electrodeposition of metals often exert their effect by selectively accelerating or inhibiting one of the competing reactions occurring at the electrode, a study was made to demonstrate the predictable effect of additives that affect the rate of electrode reactions by ion pairing, electron bridging and electrode filming. The effect of these additives was demonstrated by studying their effect on voltammetric measurements, on the current efficiencies for deposition of metals and on the composition of binary alloys. In each case it was demonstrated that one could predict, using principles taken from other areas of research, the effect of each type of additive on the rate of deposition of the different metals and one could demonstrate that, with these types of additives, the effect on current efficiency and on the composition of binary alloys could be predicted.

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT ☑ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL Robert G. Ghirardelli	22b. TELEPHONE (Include Area Code) (919) 549-0641	22c. OFFICE SYMBOL USARO

DD FORM 1473, 84 MAR 83 APR edition may be used until exhausted.
All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE
UNCLASSIFIED

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Abstract

Using the principle that additives used in electrodeposition of metals often exert their effect by selectively accelerating or inhibiting one of the competing reactions occurring at the electrode, a study was made to demonstrate the predictable effect of additives that affect the rate of electrode reactions by ion pairing, electron bridging and electrode filming. The effect of these additives was demonstrated by studying their effect on voltammetric measurements, on the current efficiencies for deposition of metals and on the composition of binary alloys. In each case it was demonstrated that one could predict, using principles taken from other areas of research, the effect of each type of additive on the rate of deposition of the different metals and one could demonstrate that, with these types of additives, the effect on current efficiency and on the composition of binary alloys could be predicted.

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Final Report on Control of the Composition

of Electrodeposited Alloys by the Use of

Certain Types of Additives

A. Statement of the Problem

Additives used in electrodeposition processes are, in most papers, visualized as either complexing agents or relatively inert agents that merely block reactions at the electrode. The purpose of this study was to demonstrate that it was possible to predict the action of additives acting by totally different mechanisms by utilizing physical and chemical properties known from their behavior in other types of processes. Utilizing the predicted mechanisms of reaction, studies were made of the effects of the additives on the rates of deposition of different metals as shown by voltammetric curves, current efficiencies and composition of binary electrodeposited alloys.

In this phase of the overall project three mechanisms were predicted and studied. These were:

(1) Ion pairing--Metals are deposited from neutral, positive or negative ions on a negatively charged cathode. In cases where the rate of deposition is controlled by diffusion or convection the charge interaction has no influence on the rate of deposition

but in cases where the rate of deposition is controlled by adsorption the charge on the depositing ion exerts an appreciable effect. Thus, when a negative ion is adsorbing on the negative cathode there is a repulsive force slowing down the reaction. If one adds a large positively charged ion it will ion pair with the negative ion, decreasing the charge on the depositing ion, thus, decreasing the repulsive force and increasing the rate of deposition. However, if the depositing ion is positively charged the positively charged additive will not ion pair and thus one should observe no acceleration of the rate of deposition. When alloy deposition occurs from solutions containing one metal present in a negative ion and one present as a positive ion, addition of an ion pairing cation will cause an increase in the percentage in the alloy of the metal deposited from negative ions. In cases where one deposits the metal from a negatively charged ion, where the deposition reaction competes with the evolution of hydrogen from a positively charged hydronium ion or neutral water, one should observe an increase in current efficiency for the deposition of the metal upon addition of the ion pairing cation.

(2) Ion bridging--A number of ions have been shown to catalyze electron transfer reactions in both homogenous and electrolytic processes by serving as electron bridges. These ions would be expected to serve also as electron bridges for the electroplating of a number of metals. This bridging should be most probable

with ions that complex with the metal ion and that have electron clouds that can be easily polarized. It would be expected that using this type of additive should increase the current efficiency for deposition of metals with which they can form bridges and should increase the percentage of this metal in electrodeposited alloys.

(3) Electrode filming- It is known that film formation is important in chromium plating and anomalous codeposition of alloys but there has been no systematic study of using films to control the rates of electrodeposition processes. It would be expected that the formation on the electrode of a conductive, insoluble film containing a metal ion would inhibit the reduction of other ions on that electrode and would correspondingly produce alloys richer in the metal forming the insoluble film and should increase the current efficiency for deposition of that ion.

B. Summary of Results

1. Reviews of Previous Work.

In the preliminary stages of the project the mechanisms of action of additives in electrodeposition processes were reviewed. This review concentrated on mechanisms that had not been covered extensively before. Thus it omitted discussion of electrode blocking, simple complexing and electrostatic effects in the double layer. These three mechanisms have been extensively

discussed and have been utilized as the major explanations in the majority of electrodeposition experiments in which explanations have been given. This review was presented in an invited paper in a symposium on "Additives in Electrodeposition Processes" at the Fall, 1985 meeting of the Electrochemical Society in Las Vegas, Nevada (8)* and as a part of a more general invited paper at the "6th International Symposium on Surfactants in Solution" in Summer, 1986 in New Delhi, India (13). These papers have been published or are in press.

2. Ion pairing effects on electrodeposition.

It has been demonstrated that ion pairing is a basic mechanism by which quaternary ammonium salts affect the rate of electrodeposition processes and that addition of quaternary salts:

(a) Do not affect the rate of deposition of transport controlled electrodeposition processes.

(b) Do not accelerate the rate of deposition of metals that are deposited in a reaction in which the rate determining step is adsorption of positively charged ions. In fact, because the quaternary salt also blocks the surface of the electrode, there is usually a slight inhibition of the rate of deposition of these

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*The reference numbers refer to the list of publications and oral presentations at the end of the report. A more complete list of pertinent references are given in the listed journal articles, especially in Reference 1.

metals.   This has been demonstrated in the evolution of hydrogen and in the deposition from aquated thallium(I) and the ethylene diammine complexes of copper(II) and nickel(II).

(c)   Do accelerate the rate of deposition, in adsorption limited processes, of metals deposited from negatively charged ions. This has been demonstrated utilizing deposition of tin from stannite and stannate solutions, zinc from zincate solution and cadmium from the cyanide complex.

(d)   Do, in the cases described in (c), have their increase in rate increased still more by changing the solution conditions in a manner that would be expected to increase the amount of ion pairing.   Thus, addition of tert-butanol to the aqueous stannate solution containing a quaternary salt would be expected to increase the amount of ion pairing between the quaternary salt and the stannite ion and this did result in a further increase in the rate of deposition of the stannite ion.

The effects described above were shown by three different experimental techniques:

(a)   Voltammetry: The presence of ion pairing by quaternary ammonium cations involving the negative ions that were discharging caused an increase in the limiting current region of the voltammetric curve, while the absence of ion pairing when the reacting ions were positive, was shown by the absence of an increase in the limiting current.   The inhibition, by the

quaternary salt, of hydrogen evolution was shown by the decrease
at a fixed potential of the current in the hydrogen evolution
region of the curve.

(b) Current efficiency--Since the quaternary salts slightly
inhibited hydrogen evolution and reduction of non ion-pairing
metal complexes but accelerated the rate of deposition of metals
from negatively charged ions, addition of the quaternary salt
caused an increase in the current efficiencies for deposition of
the ion deposited from anions and little or no change in current
efficiencies for deposition of metals deposited from cations.

(c) Alloy composition--Since addition of the quaternary salts
caused no effect or a slight inhibition when the metal was
deposited from a positive ion while it caused an increase in the
rate of deposition of a metal deposited from negative ions,
addition of the quaternary salt caused an increase in binary
electrodeposited alloys, of the percentage of the metal deposited
from anions.

This effect was demonstrated with tin/copper, zinc/thallium,
tin/thallium, tin/nickel and cadmium/thallium alloys where the
first metal listed was deposited from a negative ion.

These results on ion pairing were published in one paper
supported by this grant(4), one paper not supported by this
grant(21) and was presented in two oral papers(9,11).

3. Ion pairing effects on hydrogen embrittlement.

It has also been demonstrated that adding quaternary ammonium
salts will decrease the hydrogen embrittlement observed when

depositing cadmium from cyanide baths on iron wires. This effect has been traced to two ion-pairing effects.

(a) Effect on current efficiency--As described in Section (2), because the cadmium is deposited from a negatively charged cyanide ion, one would expect that addition of a quaternary salt to the bath would increase the current efficiency and experimentally this was observed to be true.

(b) Effect on rate of absorption of hydrogen--The rate of absorption of hydrogen has previously been demonstrated to be accelerated by strong adsorption of negative ions, like cyanide, arsenite, and bisulfide. A reasonable explanation for this is the repulsion of the negative hydride ion in the surface layers of iron by the layer of negatively charged ions. If this is true, adsorption of quaternary ions on the metal surface should, by ion-pairing with the cyanide, decrease this repulsion causing a decrease in the rate of absorption of hydrogen. Experimentally this was demonstrated to be true.

It was demonstrated, utilizing the bend test, that addition of quaternary salts did decrease hydrogen embrittlement.

The results of this study are at present being published(6). The manuscript is attached in Appendix I.

4. Ion bridging effects on electrodeposition.

As reported(3,10) it has been demonstrated that the thiocyanate ion acts as an electron bridge accelerating the rate of deposition of cobalt and nickel but not accelerating the rate

of deposition of hydrogen or lead. Because bridging is an effect on the energy barrier for electron transfer these effects were observed as shifts of the half wave potential. The limiting current was not changed. The bridging effect was also observed as the cause of an increase in the current efficiency for the deposition of nickel and cobalt and a decrease in current efficiency for deposition of lead. It was also observed that in deposition of binary lead alloys addition of thiocyanate increased the percentage of nickel and cobalt.

This approach to controlling the relative rates of competing electrolytic processes has not been pursued since a parallel research project, not supported by this grant, has shown that measurements of volumes of activation for the deposition process is a much more specific tool for identifying and understanding the role of electron bridging additives(16-20).

The measurement of volumes of activation has furnished a method of determining the number of ligands lost in the deposition process in order for electron transfer to occur. Thus it was shown that in order for fully aquated nickel(II) and cobalt(II) ions to be reduced two water molecules had to be removed, one from the ion and one from the surface of the electrode. If chlorides are added to the solution, it is only necessary to lose one water molecule in order to transfer the electron. Apparently, the chloride acts as an inner sphere electron bridge. Probably, the chloride bridge originates as an

adsorbed chloride on the electrode and the water is lost from the aquated ion.

If thiocyanate or azide ions are added to the solutions containing the fully aquated cobalt and nickel ions the volume of activation drops to zero. These ions apparently form outer sphere bridges making it unnecessary for the loss of any solvent molecules before electron transfer can occur. Apparently the π electron clouds of these anions are able to bridge around the water molecules.

Saturated aliphatic sulfonates added to solutions of aquated nickel ions served only as blocking agents. There was no indication of bridging. However, unsaturated aliphatic and aromatic sulfonates caused lowering of the volume of activation showing the presence of electron bridges formed through the π clouds.

In the electrodeposition of silver there are no comparative values to determine exactly how many solvent molecules are lost when depositing silver from the fully aquated ion. However, introduction of cyanide ions causes the volume of activation to drop to zero showing that cyanide ions with their π clouds serve as outer sphere electron bridges.

5. Electrode Filming

It is felt that the work on ion pairing and ion bridging has proceeded far enough to establish the general areas in metal electrodeposition in which one can utilize and expect to find

these effects. However, it is felt that the most drastic effects are observed when insoluble films are formed on the electrodes and this field has only been lightly touched. One article has been published(5) describing the ability of surfactants to form multilayer films similar to Langmuir-Blodgett films resulting in periodic increases and decreases in the current efficiency for cobalt deposition as the film alternately changed its character from hydrophobic to hydrophilic. In addition two oral presentations (12, 15) reported on the following projects now under way. These projects will continue and be carried to a conclusion after the close of this grant.

(a) Copper Deposition-The objective in the copper work was to demonstrate the effect of formation, during deposition, of a film containing the metal ion to be deposited. Copper(II), upon reduction, produces copper(I) which forms a number of insoluble salts. Thus, if one is depositing copper, addition of anions such as chloride, bromide, iodide and thiocyanate would be expected to cause an insoluble precipitate to form during the deposition. This film would be expected to interfere with the rate of reduction of other ions at the electrode in the same manner as the accepted mechanism for anomalous deposition of alloys. On the other hand one would not expect this type of an effect in the evolution of hydrogen or the deposition of metals like cadmium when one adds chloride, bromide, iodide and thiocyanate. Thus, one would expect that addition of these anions should cause:

(1) Increases in the current efficiency for deposition of copper from copper(II) baths. This should occur because formation of the film should interfere with and decrease the rate of deposition of hydrogen while they should cause only small effects on the rate of deposition of copper.

(2) Little or no effect on the current efficiency for deposition of metals like cadmium which do not precipitate insoluble halides since the film will not be formed in this deposition.

(3) Increases in the percentage of copper in electrodeposited binary alloys of copper and a metal that does not form insoluble halides. In these cases the insoluble halide will interfere with and decrease the rate of deposition of the second metal but not interfere with the deposition of copper.

EXPERIMENTAL DETAILS

Current efficiency--Current efficiencies were determined by weighing deposits formed by electrodeposition at 0.050 amps for 1.5 hours on $18cm^2$ copper cathodes. The plating solutions were 0.1M in sodium sulfate, 0.04M in H_2SO_4 and 0.010M in copper sulfate. In some experiments the anode and cathode compartments were separated with a porous porcelain cup. Deposition was performed using an Anotrol 4700 Potentiostat.

Alloy Deposition--The alloys were deposited using basically the same equipment and conditions used in the current efficiency

studies with the exception that the alloys were plated on lead rather than copper cathodes. The concentration of zinc nitrate and cadmium sulfate in the solution was 0.01M. The deposits were analyzed using a Norelco X-ray spectrometer.

RESULTS AND DISCUSSION OF RESULTS

The results are summarized in Table I - III.

TABLE I
The Effect of Halides and Thiocyanate on the Current
Efficiency for Deposition of Copper from a Copper Sulfate
Solution

Additive		No of Runs	% Current Efficiency	Precision
None		5	67.7	±3.2
0.1mM	NaCl*	2	69.7	±2.0
1mM	NaCl	3	79.6	±2.1
10mM	NaCl	5	70.0	±1.7
6 M	NaCl	2	68.3	±1.6
1mM	KSCN	6	75.6	±0.7
1mM	NaBr	5	66.9	±4.8
1mM	NaBr*	2	78.9	±1.5

*These runs were made with separated anode and cathode compartments. The other runs were made with both electrodes in the same compartment.

TABLE II

The Effect of Halides and Thiocyanate on the Current Efficiencies for the Deposition of Zinc and Cadmium

Solution Composition	No of Runs	% Current Efficiency	Precision
10mM $Zn(NO_3)_2$ [A]	3	25.2	±1.4
[A]+ 10mMNaCl	3	24.8	±1.9
[A]+ 1mM NaBr	3	22.7	±1.8
[A]+ 1mM KSCN	3	23.3	±1.4
10mM $CdSO_4$ [B]	3	57.4	±1.7
[B] + 10mM NaCl	3	61.1	±7.7
[B] + 1mM NaCl	3	51.5	±2.5
[B] + 1mM KSCN	3	61.7	±2.5

TABLE III

The Effect of Halides and Thiocyanate
on the Weight Ratio of Metals Plated in Binary Alloys

Ratio of	Additive	No of Runs	Weight Ratio	Precision
Cu/Zn	None	3	61	±0.1
Cu/Zn	0.1mM NaCl	4	170	±14
Cu/Zn	1 mM NaCl	4	141	±3
Cu/Zn	10 mM NaCl	4	266	±3
Cu/Zn	1 mM KSCN	3	.162	±17
Cu/Zn	1 mM NaBr	3	193	±3
Cu/Cd	None	3	2.78	±0.8
Cu/Cd	1 mM NaBr	3	4.07	±0.7

It can be seen in Table I that, as expected, addition of small concentrations of sodium chloride cause increases in the current efficiency for copper deposition. This effect reaches a maximum at 1mM sodium chloride. At 6M sodium chloride it has decreased until it is essentially the same as was obtained without additive. This behavior was expected since, in addition to the formation of an insoluble film, chloride also complexes with copper(I) and (II). It was expected at high concentrations of chloride that the copper(I) chloride would dissolve and this would eliminate the effect of the film on the electrode.

It is somewhat surprising that the maximum in the effect occurs at around 1mM sodium chloride indicating that complexing of the copper(I) on the electrode begins at this small concentration. This is probably attributable to the fact that at the electrode, because the chloride is strongly adsorbed on copper, the chloride concentration is much higher than it is in solution.

It can also be seen that 1mM sodium chloride, sodium bromide (in a separated cell), and potassium thiocyanate all show essentially the same effect (79.6%, 78.9% and 75.6% respectively). This is also reasonable from the model that the effect, in all cases, is merely physical blocking of the electrode by formation of insoluble films of the copper(I) salts.

It can also be seen that the increase in current efficiency is not observed when bromide is the additive and the anode and cathode are in the same compartment. If, however, one separates the anode and cathode compartments one observes the expected rise in current efficiency. This shows clearly the effect on the cathodic process of the bromine generated at the anode.

In Table II one can see that addition of these anions causes no large increase in the current efficiency for deposition of cadmium and zinc. In fact in several cases there are decreases in the current efficiency. This lack of an increase is to be expected since these anions do not form insoluble compounds with these metal ions.

Table III shows that the effect of the additives on the composition of electrodeposited alloys. One can see clearly that the copper/zinc ratio jumps upon introduction of the additive from 61 to values in the range of 140-266 and the copper/cadmium ratio jumps from 2.8 to 4.1. One does not observe. the decrease in the effect that was observed in the current efficiency measurements at any of the additive concentrations used. However, the effect was not one researched since it was felt that the codepositing cadmium and zinc would cover some of the insoluble film and that there would not be time enough for the complexing reaction to occur.

Conclusions

It was demonstrated in the case of copper and some of its alloys that additives that cause precipitation of insoluble copper(I) salts cause increases in current efficiency for copper deposition and not for metals that do not form insoluble salts; they also cause in the electrodeposition of binary alloys increases in the ratio of the amount of the copper to the amount of metal that does not form insoluble precipitates.

(b) Lead Deposition

The rate of electrodeposition of lead from a plumbite solution in 2N sodium hydroxide is sensitive to the rate of stirring showing that the normal rate of deposition is transport limited. However, preliminary experiments indicated that a film was formed on the electrode surface. It was concluded that this film dissolved readily in the 2N sodium hydroxide and thus, under normal conditions, one probably did not observe any effects from this film. It was concluded that one could observe effects of this film if one could protect the film from the rapid corrosion reaction. An investigation was then made of the possibility of protecting this film with a surfactant film.

EXPERIMENTAL DETAILS

Voltammetric measurements were made with an EG&G Model 362 Potentiostat. The cell contained platinum working($11.2mm^2$) and counter electrodes with a saturated calomel reference electrode (SCE). All voltages are referred to the SCE. The concentration of the metal ions was $1.0X10^{-3}M$.

Current efficiencies were determined from the weight of the deposit obtained from galvanostatically depositing the lead at 50mA on $18cm^2$ copper electrodes for two hours using an Anotrol 4700 potentiostat. The additive used was tetrabutylammonium perchlorate (TBAP). The lead concentration was 0.01M.

Alloy deposition studies were performed using the same experimental arrangement and solutions used for current efficiency measurements. The alloys were analyzed using a Novascan 30 Scanning Electron Microscope with a Princeton Gamma Tech System IV, X-ray fluorescence analyzer or a Phillip PW 1720 X-ray Generator.

RESULTS AND DISCUSSION OF RESULTS

Voltammetric Studies

Voltammetric curves using sweep rates of 20MV/s for lead deposition in basic solutions showed that when the voltage was not allowed to sweep past 0.5V (the potential at which a second reaction occurred) the curve was reproducible except for the expected gradual increase in the height of the wave caused by

increases in surface area as the lead deposits. However, when the voltage is allowed to sweep into the region of the second reaction one could observe a shift of the half wave potential in the positive direction. After several runs a prewave developed. It was concluded that the loss of water in the surface film in the second reaction caused an insoluble film to form on the electrode. This film was isolated by electrolyzing the lead solution in a sandwich cell(1) where there is a limited amount of water. X-ray diffraction of the solid film showed it to be $Pb_6O_5(NO_3)_2$. A film of this type would be expected to be formed by denydration and ionization of the lead hydroxide. It should be pointed out that this is the same type of film that has been concluded to be formed in the electrodeposition of chromium.

One can clearly see the effect of addition of tetrabutylammonium perchlorate (TBAP) if one obtains voltammetric curves at 200mv/s [The high sweep rate was used since it was felt that this more clearly reflects the conditions in actual plating where the depositing metal is rapidly covering the surface and continually exposing a new surface and new conditions.] At this sweep rate, in the absence of the surfactant, one sees a slow build up of the film as shown by the gradual shift of the voltammetric curve in the anodic direction but upon introduction of the surfactant (Fig. 1) one sees a rapid shift in this initial portion of the curve showing a rapid and steady build up of the
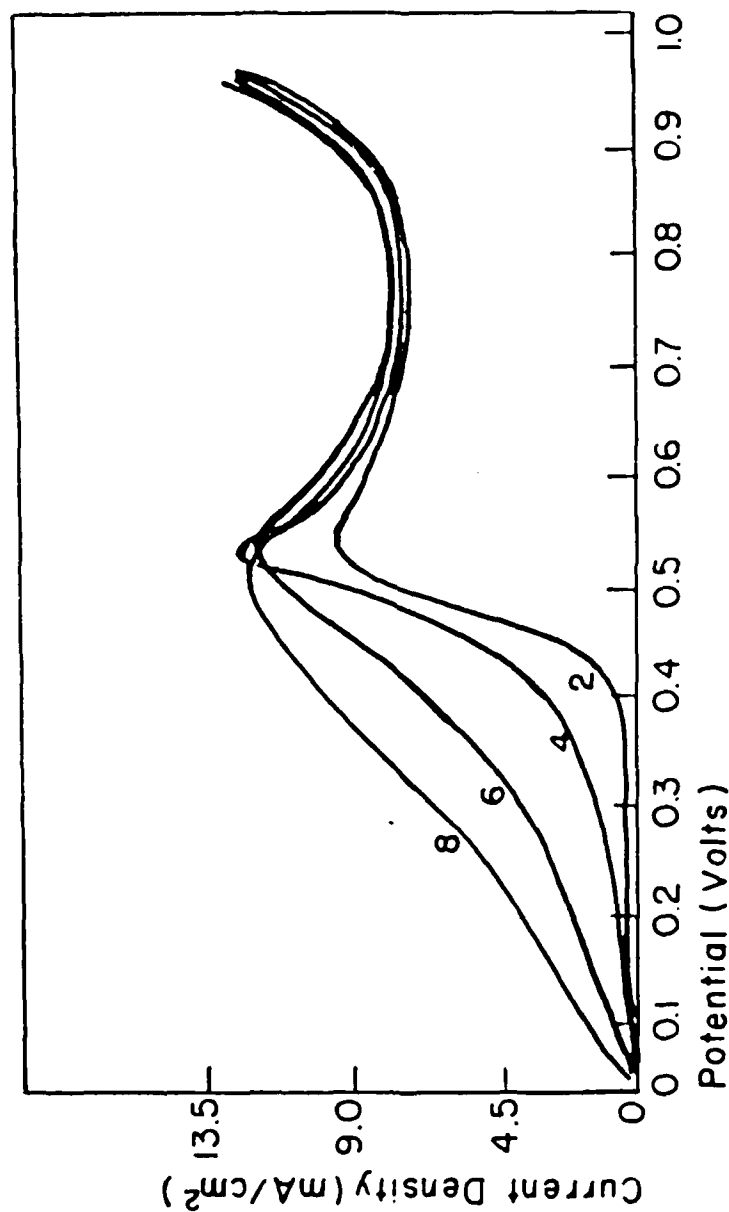
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Fig. 1 The effect of successive voltage sweeps on the voltammetric curves for deposition of lead on platinum.
(3 X 10^{-3}M Pb(NO$_3$)$_2$, 2 M NaOH, 1 X 10^{-6}M TBAP. Sweeprate – 200 mV/sec. The numbers refer to the number of the successive voltage sweeps)

film on the surface. This shows clearly the ability of the surfactant film to protect the oxide film from the corrosive action of the aqueous sodium hydroxide.

The ability of the surfactant to protect the oxide film and allow it to build on the surface should be reflected in the current efficiency and in the composition of electrodeposited lead alloys. As is observed in anomalous codeposition the presence of the lead oxide film should hinder the deposition of hydrogen or another metal and one should see an increase in current efficiency and an increase in the relative composition of lead in a binary alloy.

In current efficiency studies (Table IV) the fact that, in the absence of oxygen, the current efficiency was essentially 100% obscured any ability to observe an increase in current efficiency caused by addition of the surfactant.

Table IV
The Effect of TBAP on the Current Efficiency
for Deposition of Lead in Aqueous
2N Sodium Hydroxide

Conditions	Without Additive			With 10^{-6}M TBAP		
	No. of Runs	Effi- ciency %	Avg. Dev.	No. of Runs	Effi- ciency %	Avg. Dev.
Exposed to Air	3	71	3	4	99	1
Bubbled with O_2	1	32	-	1	50	-
Bubbled with N_2	5	105	5	4	100	0

In all cases there is some oxide codeposited with the lead. This is especially obvious in the nitrogen bubbled experiments where the extra oxide causes the current efficiency to appear to be above 100% X-ray diffraction showed the presence of oxides in the deposit.

If one has oxygen present so that the current efficiency is not close to 100% one observes a marked increase in current efficiency, both in experiments where the cell is open to the atmosphere and in those where oxygen is bubbled through the solution. In these cases there is no doubt that the surfactant increases the current efficiency. However, the exact reason is debatable. The surfactant could protect the oxide and the oxide could block secondary reactions or the surfactant could block transport of oxygen to the electrode. Probably both mechanisms are involved.

Table V shows the effect of the TBAP on the ratio of metals deposited on binary alloys. It can be seen that in all cases the presence of TBAP causes significant increases in the ratio of lead to the other metal. This was expected since it allowed the formation of the lead film which inhibited the deposition of the other metal.

TABLE V
The Effect of TBAP on the Ratio
of Lead to Other Metals in Electrodeposited Alloys

Metal Alloys	Ratios	
	Without Additive	With 10^{-6}M TBAP
A. Deposited in air		
Pb/Tl	0.48	0.73
Pb/Cu	0.35	1.0
Pb/Ni	0.89	2.53
B. Deposited in nitrogen*		
Pb/Cu	4.8	7.3
Pb/Ni	44.5	94.5

*These experiments were performed at a much later time
than those deposited in air and the stirring conditions
were quite different. This is probably the cause of a
portion of the large difference between the ratios in A.
and B. In each case though, the comparisons with and
without surfactant were made with the same stirring
conditions.

C. Thallium Deposition

The study of thallium alloy deposition is important not because there is much use for electrodeposited thallium alloys but because thallium is an additive that has been utilized in gold plating. In this process small amounts of the thallium is codeposited with the gold.

Thallium deposition alone is usually regarded as a typical example of a well behaved univalent metal in aqueous systems.

EXPERIMENTAL

Voltammetric studies were made with an EG&G Model 362 Potentiostat. The cell contained platinum working (11.2mm^2 area) and counter electrodes and a saturated calomel reference electrode (SCE). All voltages are given versus the SCE. The working electrode was rotated at 1800 rpm or the solution was stirred with a magnetic stirrer. The oxygen content was varied by plating in solutions open to the air, bubbling with oxygen, bubbling with nitrogen, or adding sodium sulfite.

Current efficiencies were determined by weighing the deposits obtained by plating at 0.05A or 0.005A on 18cm^2 copper electrodes from solutions that were either 2M sodium hydroxide or 1M potassium nitrate and 10 or 1.0 mM in thallium nitrate. In some experiments the anode and cathode compartments were separated with a porous cup. The oxygen content was increased by bubbling with oxygen and decreased by bubbling with nitrogen or adding sodium sulfite. Deposition was performed using an Anotrol 4700 potentiostat.

Alloy deposition was accomplished under the same conditions as the current efficiency measurements except that the thallium-copper alloys were plated on lead rather than copper. In each experiment the concentrations of copper nitrate, zinc nitrate and silver nitrate were equal to the concentration of thallium nitrate. Deposits were analyzed using a Novascan 30 Scanning electron Microscope with a Princeton Gamma Tech System III X-ray Fluorescence Analyzer or a Norelco X-ray Fluorescence Analyzer.

X-ray diffraction was done with a Philips X-ray diffractometer consisting of a PW 1720 X-ray generator and a Universal Vacuum X-ray Spectrograph.

EXPERIMENTAL RESULTS

Tables VI and VII summarize the experimental results.

TABLE VI

Percent Current Efficiency for Thallium Deposition.

A. 50mA, 2M sodium hydroxide

Air	N_2 Bubbled	O_2 Bubbled	Air Plus 0.07M Sulfite
85.5±1.1	100±0	0±0	100±0

B. 5mA, 2M sodium hydroxide

Air	N_2 Bubbled	Air + Sulfite 0.07M	0.035M
26±6*	26±2	30±4	---
34±3	44±5	30±3	46±1
	50±5**		

C. 5mA, 1m KNO_3

Air	N_2 Bubbled	Air + Sulfite 0.07M	4.7M
22±1*	-	38±5	49±4
18±1*	28±5		

*The two different rows of figures correspond to different stirring conditions. In each row they were stirred the same.

**Anode and cathode compartment separated. In all other cases the electrodes were in the same compartment.

Table VII
Effect of Type of Atmosphere on Alloy Composition

Alloy	Air	Nitrogen	Sulfite (0.07M)
Tl/Zn	17±5	2000±40	1400±20
Tl/Cu	0.08±0.02	0.20±0.01	--

As in the case of lead deposition, an insoluble compound is involved in the deposition of thallium. This insoluble compound is visible in the system and it was shown by X-ray diffraction to be predominantly thallium(III) oxide (Tl2O3). The mechanism of its formation was concluded to involve the reduction of oxygen, probably to produce hydrogen peroxide, and the reaction of the deposited thallium with the hydrogen peroxide produced. Thus the presence of oxygen leads to a decrease in the amount of thallium being deposited.

It can be seen in the tables that, as the amount of oxygen increased, the current efficiency for deposition of thallium decreased and the ratio of thallium to the other metal in electrodeposited alloys, decreased. The deposit in the case of thallium did not stay on the electrode but was observed to float away from the electrode surface. Thus it formed no protection for the metal surface. Because it was not on the surface addition of TBAP did not help protect the surface and, different from lead deposition, addition of TBAP caused no appreciable change in the measured quantities. Thus the current efficiency for deposition of thallium in air without TBAP was 85% while in the presence of TBAP it was 81%.

C. List Of All Publications

Refereed Publications

1. Thomas C. Franklin, "Some Mechanisms of Action of Additives in Electrodeposition Processes", Surface and Coatings Technology, 30, 415-428 (1987).

2. Thomas C. Franklin and Shaj A. Mathew, "The Use of Surfactants in Electrochemistry", in Surfactants in Solution, Edited by K. L. Mittal. Proceedings of the 6th International Symposium on Surfactants in Solution, In Press.

3. Thomas C. Franklin, John Chappel, Randy Fierro, Ali I. Aktan, and Robbin Wickham, "The Role of Ion Bridging in Controlling Competitive Electrodeposition Processes", Surface and Coatings Technology, 34, 515-522 (1988).

4. Thomas C. Franklin, Venita Totten and Ali I. Aktan, "Ion Pairing as a Mechanism of Action of Additives in Electrodeposition", J. Electrochem. Soc., 135, 1638-1640 (1988).

5. T. C. Franklin and A. I. Aktan, "The Effect of Multilayer Adsorption of Cationic Surfactants on the Electrodeposition of Cobalt", J. Electrochem Soc, 135, 1636-1638 (1988).

6. T. C. Franklin, J. Darlington and W. Daulat, "Ion Pairing as a Method of Reducing the Hydrogen Embrittlement of Iron," Surface and Coatings Technology, In Press.

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7. Thomas C. Franklin, Venita Totten and Ali I. Aktan, "The Use of
    Filming Agents to Control the Rate of Electrodeposition of
    Metals" in <u>Proceedings of the 1987 U. S. Army Chemical Research
    Development and Engineering Center Scientific Conference on
    Chemical Defense Research</u>, M. D. Rausa, Ed., CRDEC-SP-88013,
    Nov., 1987, pub. April, 1988, <u>2</u>, 633-640.

<p align="center">List of Oral Presentations</p>

8. Thomas C. Franklin, "Mechanisms of Action of Additives in
    Electrodeposition" Invited paper at Fall, 1985 Meeting of
    Electrochemical Society in Las Vegas, Nevada.

9. Thomas C. Franklin and Jerald Darlington "The Role of Ion
    Pairing Additives in Controlling the Composition of
    Electrodeposited Alloys," Fall, 1985 Meeting of the
    Electrochemical Society in Las Vegas, Nev.

10. Thomas C. Franklin, Randy Fierro and J. Chapell, "The Use of
    Anion Bridging to Control the Composition of Electrodeposited
    Alloys," Fall, 1985 Meeting of the Electrochemical Society in
    Las Vegas, Nev.

11. T. C. Franklin, V. L. Totten and A. I. Aktan, "A Study of the
    Role of Ion Pairing in Controlling the Composition of Some
    Alloys of Lead, Tin and Zinc," Fall, 1986 Meeting of the
    Electrochemical Society in San Diego, Calif.

12. T. C. Franklin, V. Totten and A. I. Aktan, "The Use of
    Filming Agents to Control the Role of Electrodeposition of
    Metals," Fall, 1987 U.S. Army CRDEC Scientific Conference at
    Aberdeen Proving Grounds, Md.

13. T. C. Franklin and S. A. Mathew, "The Use of Surfactants in Electrochemistry," 6th International Symposium on Surfactants in Solution, Summer, 1986, New Delhi, India.

14. T. C. Franklin, "The Role of Surfactants in Electrochemistry and Catalysis," 1986 Southwestern Regional Meeting of the American Chemical Society, Houston, Tex.

15. T. C. Franklin, V. Totten and A. I. Aktan, "The Use of Insoluble Films to Control the Rate of Electrodeposition of Metals," Fall, 1988 Electrochemical Society Meeting, Chicago, Ill.

PUBLICATIONS AND ORAL PRESENTATIONS IN THE SAME TIME PERIOD RELATED TO THIS PROJECT BUT NOT SUPPORTED BY THIS GRANT

16. Thomas C. Franklin and Shaj A. Mathew, "The Measurement of Volumes of Activation as a Tool for Understanding the Mechanism of Action of Additives in Electrodeposition", J. Electrochem. Soc., 134, 760-761 (1987).

17. T. C. Franklin and Shaj Mathew, "The Effect of Anionic Additives on the Volume of Activation for the Electrodeposition of Nickel," J. of the Electrochem. Soc., 135, (11) 2725-2728, (1988).

18. T. C. Franklin and Shaj A. Mathew, "The Effect of Some Additives on Volumes of Activation in the Electrodeposition of Cobalt, Nickel and Silver," Submitted to J. Electrochem. Soc.

19. S. A. Mathew and T. C. Franklin, "The Use of High Pressure Effects as a Means of Studying the Role of Additives in Electrodeposition Processes," Paper presented at the Fall, 1986 Electrochemical Society Meeting in San Diego, Calif.

20. T. C. Franklin and S. A. Mathew, "The Use of Volumes of Activation to Determine the Mechanism of Action of Additives," Paper presented at the Fall, 1988 Electrochemical Society Meeting in Chicago, Ill.

21. Thomas C. Franklin, Jerald Darlington and Randy Fierro, "Ion Pairing as a Method of Controlling the Composition of Electrodeposited Alloys," J. Electrochem. Soc., 133, 893-896 (1986).

D. List of Scientific Personnel

These people all worked on the project but a number did not receive financial help from the contract.

Thomas C. Franklin-Principal Investigator

Venita Totten-Student working towards Ph.D.

Ali I. Aktan-Visiting Scholar from Yildiz University

Danielle Beu-Undergraduate Research Student

Particia Fernandez-Undergraduate Research Student

John Chappell*-Undergraduate Research Student (Now in industry)

Robin Wickham*-Undergraduate Research Student (Now teaching in high school)

Michael Banda*-Undergraduate Research Student (Now in medical school)

Jerald Darlington-A local Junior High School teacher (Now in graduate school)

*-Received B.S. Degree

Shaj Mathew worked on a related problem but received no financial support. He received a Ph.D. in Summer/1988.

5. Bibliography

The bibliography of references to outside publications is given in the article: Thomas C. Franklin "Some Mechanisms of Action of Additives in Electrodeposition Process" Surface and Coatings Technology 30, 415-428(1987).

APPENDIX
Article in Press

Ion Pairing as a Method of Reducing the

Hydrogen Embrittlement of Iron

Thomas C. Franklin, Jerald Darlington and

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SUMMARY

A study was made of the ability of quaternary ammonium salts
to decrease the embrittlement of iron caused by electrogenerated
hydrogen in cyanide solutions, both with and without cadmium
deposition. This embrittlement decrease was attributed to the
ability of the quaternary cation to:

(1) Ion pair with the cadmium cyanide complex to accelerate
the rate of deposition of cadmium while it inhibits, by
blocking, the rate of evolution of hydrogen.

(2) Ion pair with the adsorbed cyanide thus decreasing the
ability of the cyanide to increase the rate of absorption
of hydrogen.

Ion Pairing as a Method of Reducing the

Hydrogen Embrittlement of Iron

Thomas C. Franklin, Jerald Darlington and

William Daulat

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1. Introduction

Hydrogen embrittlement of iron has been the subject of a number of investigations(1-10). Most of the studies on the role of additives in the process have concentrated on promoter anions such as sulfide and cyanide. There have been several papers on inhibitors and in some of these it has been noted that cationic surfactants act as inhibitors of embrittlement (11-18); however, little explanation has been given for this inhibition.

As a part of a series of investigations on the mechanisms by which cationic surfactants affect electrodeposition processes, a study was made of the affect of the surfactants on the different steps involved in hydrogen embrittlement in cadmium plating of iron from cyanide baths. Previous studies have indicated that there are two basic methods by which quaternary ammonium salts could inhibit hydrogen embrittlement:

1. Positively charged quaternary ammonium ions will ion pair with negatively charged ions, such as the cadmium cyanide

complex, accelerating their reduction at the negatively
charged cathode(19-20) and, at the same time, they
inhibit, because of competitive adsorption, the reduction
of positively charged or neutral species. Thus, in
cadmium deposition, the addition of quaternary salts
should accelerate the deposition of cadmium and inhibit
the deposition of hydrogen. The result has been
shown(20), as expected, to cause an increase in the
current efficiency for cadmium deposition.

2. It has been previously concluded(10) that one of the
causes of the promotion of hydrogen embrittlement by
anionic promoters is the change in potential at the
interface caused by strong adsorption of the negatively
charged promotor ions, cyanide, sulfide and arsenite.
This increases the rate of migration of the negatively
charged hydride ion into the metal.

2. Experimental Details

2.1. Voltammetric Studies.

In all voltammetric studies the measurements were made in
unstirred solutions (Stirring had no effect on the curves.)
using a two-electrode system with a Sargent-Welch Model XXI
Polarograph.

In the study of the effect of a quaternary salt on the
electrodeposition of cadmium the plating solution, although
maintained at the same ratio of cyanide to cadmium listed in
the Metal Finishing Guidebook(29), was maintained in the

concentration range used in normal voltammetric studies, 2mM

in NaCN, 0.2mM in sodium hydroxide and 0.1mM in cadmium oxide

with a pH of 9.5-10.0. When tetrabutylammonium

hydroxide(TBAOH) was used, it was 1×10^{-5}M. The iron cathode

was a 1 cm Baker Analyzed Reagent grade iron wire, cleaned

with 6M nitric acid and rinsed with distilled water. The

counter electrode was a platinum foil (20 cm^2 in area).

2.2 Determination of the rate constants for hydrogen migration into iron

The iron electrode, a 30mm long, 0.2mm diameter wire, was

polished with emery cloth and then washed with distilled water,

nitric acid (6M), distilled water, acetone and distilled water in

that order. The counter electrode was a 3.4 cm^2 platinum foil.

The procedure used to determine the rate constants for the

migration of hydrogen into iron was the same as that used in

previous studies(7-10, 30). The solution was saturated with

hydrogen by bubbling the gas through the solution for 25 minutes.

Using the polarograph, hydrogen was electrolytically generated on

the iron wire at an applied potential of -2.0V for varying times.

Hydrogen adsorbed on and absorbed in the iron wire was

electrolytically oxidized by sweeping the voltage in the anodic

direction at about 2.5 mv/sec. Fig. 1 shows a typical

voltammetric curve. It can be seen that there are two oxidation

peaks. In the previous studies(7, 30-33) it was concluded that

the first peak was caused by the oxidation of adsorbed hydrogen

while the second was caused by oxidation of absorbed hydrogen.

The area under each peak was a measure (in coulombs) of the

amount of each form of hydrogen present.

If one plots the amount of hydrogen in the second peak as a function of time, the slope of this line is the rate of absorption of hydrogen. The rate law for absorption of hydrogen was shown to be [7]:

$$\frac{d\,[Habs]}{dt} = k[Hads] \qquad \text{Eqtn. I}$$

where [Habs], the amount absorbed, is the area under the second peak and [Hads], the amount adsorbed, is the area under the first peak. As one charges the electrode with hydrogen for increasing times, one reaches a region where the surface is saturated with adsorbed hydrogen and is constant. In this region, as expected, the plot of the amount of hydrogen absorbed vs time is a straight line. By dividing the slope of the line by the amount of adsorbed hydrogen (the area under the first peak), one can obtain k, the rate constant for the absorption of hydrogen.

1.2. Bend Tests

The embrittlement of the iron wire was measured by measuring the number of bends needed to break the wire. The wire was placed between two flat pieces of sanded wood. Then it was gently bent back and forth until it broke. In each hydrogen charging, the wire was cut into four pieces and the recorded result for this experiment was the average of these tests. In the plating experiments, the wires were shorter and only one bend test was made on each wire. For each of the pieces of data recorded in the results, 6-10 completely independent runs were

made and the results were averaged. Although the results varied somewhat from worker to worker, each individual could duplicate his results reasonably well as shown by the precision given in the tables. In all cases where comparisons were to be made the bend tests were run by the same person. Thus, all of the data in Tables II A and III A were obtained by one worker and the data in Tables II B and III B were obtained by another worker.

In the studies with cadmium plated wires, two types of plating experiments were performed. In the potentiostatic experiments, the potential was controlled at-1.0V. In the galvanostatic experiments, the current was controlled at 20mA. Electrodeposition was performed on an 8cm wire for 4 hours. The plating solution used in the early studies was 1mM in cadmium sulfate, 2mM in NaOH and 20mM in potassium cyanide. The low concentrations were chosen to maintain them in the same concentration range as the voltammetric studies. A second study was made using a more conventional cadmium plating bath (29), composed of 0.17M cadmium oxide, 0.62M sodium cyanide and 0.33M sodium hydroxide with a pH of 9.8 - 10.2. The surfactant, when used, was $3 \times 10^{-2}M$.

3. Results and Discussion of Results

3.1 Effect of TBAOH on Voltammetric Curves

Since the cadmium cyanide complex is a negative ion it was expected that addition of the quaternary salt would accelerate the rate of deposition of cadmium. At the same time, since hydrogen is evolved from the neutral water, one would expect that

the quaternary cation would, if it did anything, inhibit hydrogen evolution. In Figure 2, it can be seen that this is indeed true in that the cadmium reduction wave increases in height while the hydrogen wave is shifted slightly more cathodic.

3.2 Effect of tetrabutylammonium perchlorate (TBAP) on current efficiency

A separate study has been made on the effect of the quaternary salt on the current efficiency for cadmium deposition (20). It has been shown that because the quaternary salt increases the rate of deposition of cadmium while inhibiting the rate of deposition of hydrogen the current efficiency increases from 46% without the salt to 73% upon addition of TBAP.

3.3 Effect of quaternary salts on the rate of absorption of hydrogen

Table I shows a summary of the effect of the quaternary salts on the rate constant for absorption of hydrogen as measured by the linear portion of graphs of the amount of absorbed hydrogen as a function of time. The rate constant for absorption of hydrogen was calculated by dividing the rate (the slope of the straight line portions of the plots of amount of absorbed hydrogen vs time) by the amount of adsorbed hydrogen (The measured areas under the first peak in this portion of the plot.)

It can be seen in Table I that addition of TEAP and TBAP decreased the rate constant for absorption. It should also be noted that addition of the quaternary salts actually increased

the amount of absorbed hydrogen as measured by this technique. This points to a difficulty with this measurement technique.

There are two migration processes occuring:

(1) The migration of hydrogen from the surface of the iron into the outer layer of iron. This outer layer is probably only a few atoms thick since, within the first 10 seconds, even before the amount of adsorbed hydrogen becomes constant, one observes a rapid increase in the amount of absorbed hydrogen which is assumed to be caused by the absorption in this outer layer. The rate of absorption then slows down sharply and begins to be related to the amount of adsorbed hydrogen.

(2) The migration of hydrogen from the outer layer of iron into the interior of the iron. This is the process being studied by this technique. The recorded rate constants were obtained from the rate of increase in absorbed hydrogen after the amount of adsorbed hydrogen had reached a steady state.

The measured amount of absorbed hydrogen includes the amount in the outer layer and in the interior. It is the rise in the first few seconds that causes the measured amount of absorbed hydrogen to be high. Thus, addition of the quaternary salt decreases the repulsive force both on the surface and in the outermost layers. This allows the amount of hydrogen in the outermost layers to increase. The increase in total amount of absorbed hydrogen is caused entirely by the increase in the

amount of absorbed hydrogen that occurs within the first ten
seconds.

3.4 Effect of Tetralkylammonium salts on bend tests

The final test was the composite effect of the quaternary
cations on the embrittlement of the iron wires as measured by a
simple bend test. As demonstrated above, by ion pairing, the
cationic surfactant:

(1) Decreased the rate of migration of hydrogen into iron in
the presence of cyanide.

(2) Accelerated the rate of deposition of cadmium in a
cyanide bath while inhibiting slightly the rate of
evolution of hydrogen.

The first effect should cause a decrease in the embrittlement
of iron wires charged with hydrogen in a solution containing
cyanide. Chart I shows that this is true. The average deviation
was quite consistent at about 0.6 for each series of runs.

In Table II one can see the sharp decrease in the number of
bends caused by the presence of the cyanide and one can see the
rise in these numbers caused by addition of either of the
tetralkyl salts. It is also seen that the decrease in the
cyanide effect is greater at higher concentrations of the
quaternary salt.

In the electrodeposition of cadmium both the effect on
plating and the effect on rate of absorption should be present
and one should see a larger effect. That this is true can be
seen in Table II. This effect of the quaternary salt is the same

in both the dilute and concentrated cadmium solutions. These embrittlement test results verify the previous observations (11-18) that quaternary salts added to certain baths decrease hydrogen embrittlement.

4. Summary

It has been shown that the addition of tetralkylammonium salts decrease the promotional effect of cyanide on hydrogen embrittlement in cadmium plating because:

(1) The rate of cadmium plating is accelerated while the hydrogen evolution rate is inhibited because the quarternary salt ion pairs with the negative cadmium-cyanide complex.

(2) The ion pairing of the quaternary salt with the adsorbed cyanide ion decreases the ability of the cyanide ion to promote absorption of hydrogen.

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Although hydrogen in the transition metals is commonly referred to as hydrides there has been a good deal of debate about whether the absorbed hydrogen was neutral, positive or negative in charge (21-24). In general, transport properties are described by using the proton as a model while static properties are described in terms of anion models (21). On the other hand, many of the hydrogen embrittlement workers explain their results in terms of neutral interstitial hydrogen (24-25). In a portion of the present study, the hydrogen is regarded as a negative hydride or at least as the negative end of an Fe-H dipole. The use of the negative hydride ion here seems best to agree with the previous study (10) on the effect of applied potential and anionic additives on the rate of absorption of electrolytically generated hydrogen by iron. The negatively charged hydride ion has also been concluded to be the predominant embrittling species of room temperature in a series of studies by Ficalora et al. (26-28)

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Table VIII

Effect of Surfactants on the Rate Constants for
Absorption of Hydrogen in 2M Sodium Hydroxide

Additive	Range of Adsorbed Hydrogen (µC)	Range of Absorbed Hydrogen (µC)	Rate Constant for Absorption of Hydrogen (sec^{-1})	Avg. Deviat of the Me
0.2 mM KCN	65 - 122	52 - 175	0.053	0.008
0.2 mM KCN 2µM TEAP	84 - 148	205 - 275	0.029	0.001
0.2mM KCN 20µM TBAP	100 - 150	542 - 586	0.016	0.001

Table IX

The Effect of Tetraalkyl Ammonium Salts
on the Number of Bends
Needed to Break the Iron Wire

A. Charged in 2M NaoH

Additives	Number of Bends	Avg. Dev. Means
W/O Cyanide or Additive	11.2	0.6
0.02mM KCN	6.0	0.6
0.02mN KCN 2µM TBAP	8.3	0.6
0.02mM KCN 2µM TEAP	7.9	0.5
0.02mM KCN 2mM TEAP	10.0	0.7

B. Charged In 0.3M NaOH

Additives	Number of Bends	Avg. Dev. Mean
W/O Cyanide or Additives	11.2	0.6
0.62M Cyanide	5.2	0.5
0.62M Cyanide, 30mM TEAP	9.7	0.7

Table X
Effect of Tetraethylammonium Perchlorate on the Number of Bends Needed to Break Iron Wires Plated With Cadmium from Cyanide Solutions

A. 1mM $CdSO_4$, 2mM NaOH and 2mM KCN

Additive and Conditions	No. of Bends	Avg. Dev. Mean
No Additive, Potentiostatic	5.3	0.7
0.1mMTEAP, Potentiostatic	9.6	0.6
No Additive, Galvanostatic	5.0	0.5
0.1mM TEAP, Galvanostatic	8.8	0.8

B. 0.17M CdO, 0.62M NaCN, 0.33M NaOH

Additive and Conditions	No. of Bends	Avg. Dev. Mean
No Additive, Potentiostatic	4.4	0.6
30mM TEAP Potentiostatic	8.8	0.6
No Additive, Galvanostatic	3.9	.6
30mM TEAP, Galvanostatic	8.1	.7

List of Figures